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To be presented at the 9th International Symposium On
Reactivity of Solids, Krakow, Poland, September 1980

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BY REACTION OF CaO WITH WATER VAPOR¹

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January 1980

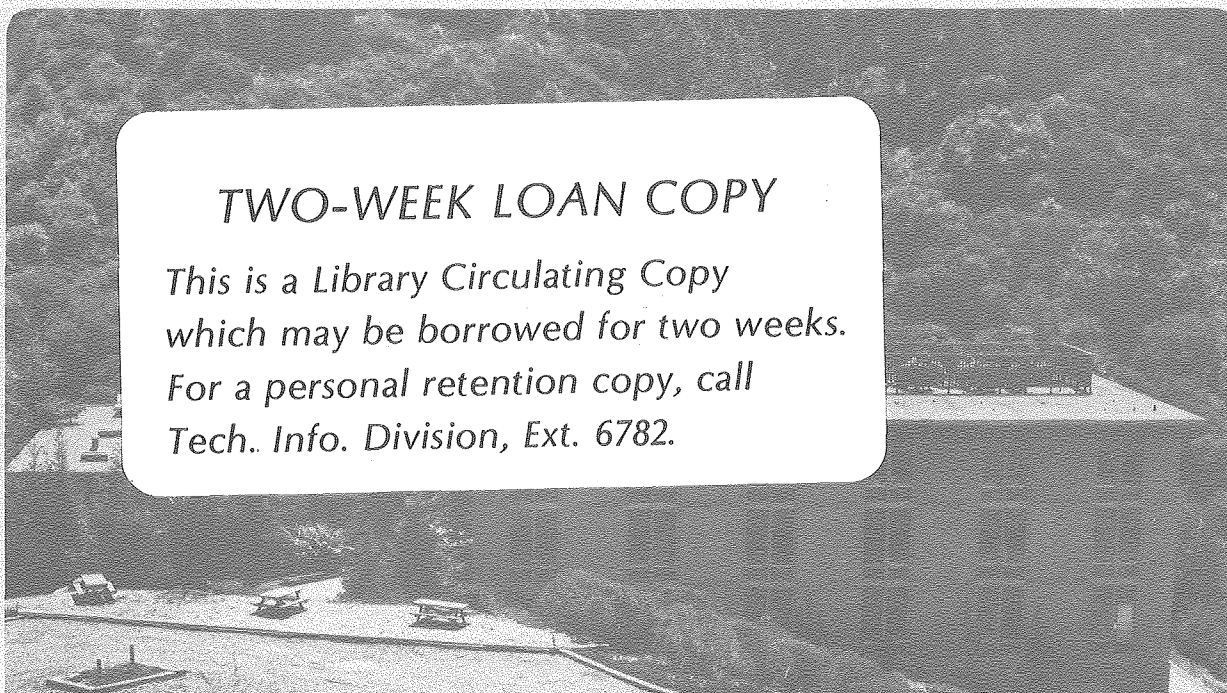
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STRAIN INDUCED PHENOMENA IN Ca(OH)_2 MADE
BY REACTION OF CaO WITH WATER VAPOR¹

Dario Beruto,^{**†} Alan W. Searcy,^{*} Luigi Barco[†] and Gabriele Belleri[†]

^{*}Materials and Molecular Research Division, Lawrence Berkeley Laboratory and Department of Materials Science and Mineral Engineering, University of California, Berkeley, California, USA; Laboratorio di Chimica, Facoltà di Ingegneria, Università di Genova, Italy

ABSTRACT

Three physically distinguishable, poorly crystalline forms of Ca(OH)_2 which are made by reactions of water vapor at 25°C with CaO powders evolve heat and develop sharper X-ray diffraction patterns when heated to 300°C. Measurements of X-ray diffraction peak line breadths, surface areas, porosities, and pore size distributions were made before and after heat treatment.

The exothermic process of the one of these forms of Ca(OH)_2 which is nonporous is recrystallization of the highly strained solid to essentially unstrained crystals. The exothermic process in two porous forms of Ca(OH)_2 , not only reduces their internal strains, but also reduces their surface areas and porosities.

¹Research supported by the Division of Materials Science, Office of Basic Sciences, U. S. Dept. of Energy under Contract No. W-7405-Eng-48 and by the Italy-U. S. Exchange Program of the Consiglio Nazionale Delle Ricerche and the National Science Foundation.

When CaCO_3 or Ca(OH)_2 powder is decomposed in vacuum, CaO is produced as particles which scanning electron microscope (SEM) pictures show to have nearly the same exterior shapes and dimensions as do the parent particles. [1,3] These CaO particles, however, have high internal porosities and in consequence, react very rapidly at room temperature with water vapor to yield porous Ca(OH)_2 particles which also appear in SEM pictures to be little changed from their grand-parent CaCO_3 or Ca(OH)_2 particles. [2]

Beruto and Searcy observed that when sr- Ca(OH)_2 (the Ca(OH)_2 produced from the reaction sequence that begins with CaCO_3 decomposition in vacuum) is heated to $\sim 290^\circ\text{C}$, heat is evolved and the X-ray diffraction (XRD) pattern sharpens. [3] It is important to learn more about the physical changes that accompany these phenomena because those changes might influence the usefulness of CaO in industrial applications which expose it to water vapor.

We here report and interpret the effects that heating has on XRD line breadths, particle morphologies, surface areas, porosities, and pore size distributions for sr- Ca(OH)_2 , for h- Ca(OH)_2 , which is made by reacting water vapor with the porous CaO that is produced by dehydration of Ca(OH)_2 in vacuum, and for is- Ca(OH)_2 , an internally strained, nonporous Ca(OH)_2 powder.

Each of the three forms of Ca(OH)_2 was made by reacting the appropriate form of CaO at 25°C with water vapor at 500 Pa pressure in a thermogravimetric adsorption apparatus. Adsorption and desorption isotherms were measured with N_2 gas at 78°K . The samples were heated without removal from the apparatus to 300°C for 30 minutes in an H_2O - and CO_2 -free atmosphere of N_2 gas, and isotherms were remeasured. No significant change in sample weight resulted from the thermal treatment. Integral line breadths of the (101) hexagonal peak of Ca(OH)_2 were measured for representative samples before

and after the thermal treatment.

The effect of temperature on the surface area of sr-Ca(OH)_2 was followed as a function of temperature by heating samples to successively higher temperatures in a Quantachrome Corp. BET apparatus for 40 minute periods in flowing N_2 gas. Surface areas measured with the apparatus were within 5 to 8% of areas obtained from the adsorption isotherms. Purities of the CaO samples, further details of experimental techniques, and methods used to calculate porosities and pore size distributions are described in other publications. [1,2,5]

The thermal treatment causes all three forms of Ca(OH)_2 to evolve heat and causes the integral line breadths (in radians $\times 10^3$) to change for sr-Ca(OH)_2 from 22.5 to 13.5, for h-Ca(OH)_2 from 23.4 to 17, and for is-Ca(OH)_2 from 16.6 to 2.9.

For is-Ca(OH)_2 , the integral line breadth after heating is smaller than that measured for $\sim 1 \mu\text{m}$ crystals of Ca(OH)_2 grown from aqueous solutions. [2] The surface area of is-Ca(OH)_2 is low, $\sim 3 \text{ m}^2/\text{g}$, and is not measurably changed by the heat treatment. The exothermic process undergone by is-Ca(OH)_2 must be recrystallization of highly strained Ca(OH)_2 to form essentially strain-free crystals.

For sr- and h-Ca(OH)_2 , not only reductions in internal strain, but also reductions in surface areas and internal porosities are produced by the heat treatment. The porosity of sr-Ca(OH)_2 decreases from 9.8 to $6.5 \text{ mm}^2/\text{g}$ and the surface area decreases from 35 to $18 \text{ m}^2/\text{g}$. For h-Ca(OH)_2 , the corresponding decreases are from 5.9 to $4.6 \text{ mm}^2/\text{g}$ and from 16.5 to $11.5 \text{ m}^2/\text{g}$.

Fig. 1 shows the effect on the surface area of sr-Ca(OH)_2 of being heated to various temperatures for 40 minute periods. The fact that heating beyond 320°C causes no further reduction in surface area implies that the driving force for reduction in surface area is low when surface areas drop below $20 \text{ m}^2/\text{g}$.

Fig. 2 shows the effect of heating to 300°C on the pore size distribution of h-Ca(OH)₂. The effect of heating on sr-Ca(OH)₂ is similar to that for h-Ca(OH)₂ in that the smaller pores are preferentially eliminated and in that pores with cross-sections less than ~3 nm are not present either before or after heat treatment. Perhaps very small pores are rapidly eliminated by surface diffusion, but reductions in porosity that accompany the heat treatment can only be accomplished by movement of atoms in the interior of Ca(OH)₂ crystals by diffusion or by cooperative processes such as movement of dislocations. [4]

If the reasonable assumptions are made a) that the line broadening measured for the Ca(OH)₂ which is produced by heating is-Ca(OH)₂ is entirely instrumental and b) that broadening due to strain is negligible in sr- and h-Ca(OH)₂ after heating, a standard method [6] can be used to calculate that their crystal dimensions average 14 and 11 nm. These results are consistent with the facts that the porous particles from which sr-Ca(OH)₂ is made are aggregates of ~10 nm diameter CaO [7] needles and that the pores in sr- and h-Ca(OH)₂ remain too small to observe by SEM even after heat treatment.

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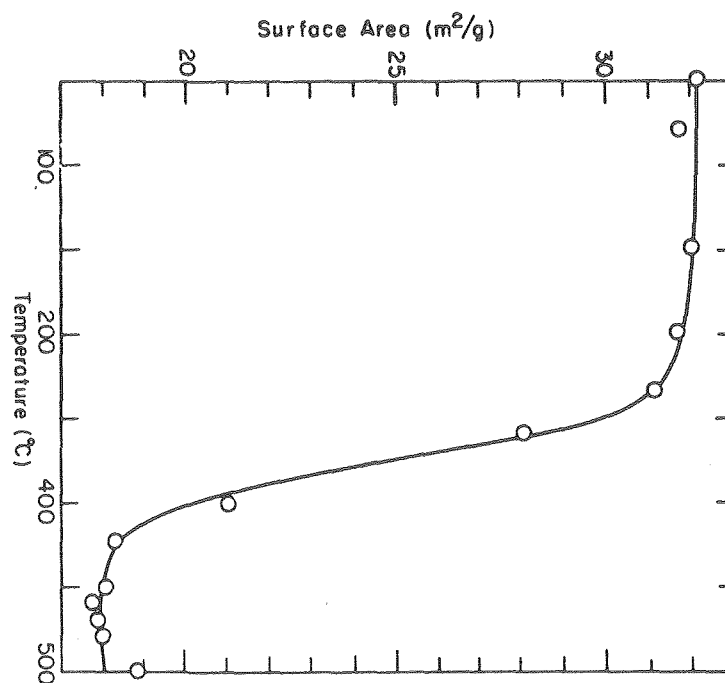


Fig. 1: Effect of heating on surface area of sr-Ca(OH)₂.

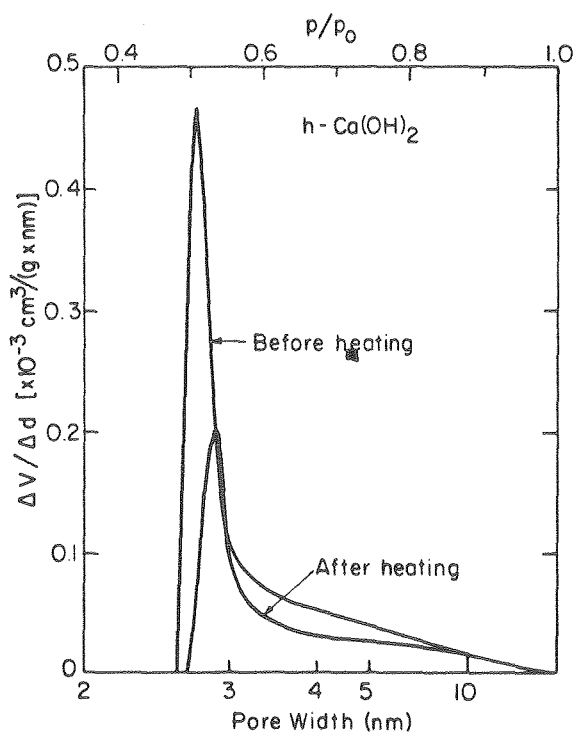


Fig. 2: Ratio of pore volume to pore width ($\Delta V / \Delta D$) as a function of pore width for h-Ca(OH)₂.

